

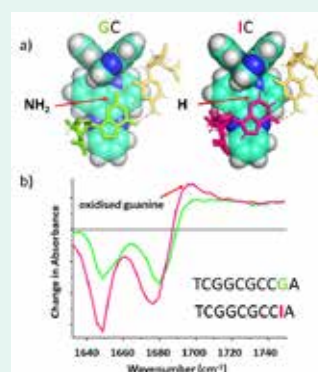
# Imaging & Dynamics for Physical & Life Science

## Time-resolved studies reveal that DNA photo-oxidation by a Ru(II) polypyridyl complex is highly sensitive to the presence of modified bases

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Small changes in DNA structure, such as occur in point mutations or base-pair mismatches, can have significant biological effects. There is therefore great interest in developing molecules that can target specific base sites in DNA. Here we have studied the photo-oxidation of DNA by an intercalating ruthenium complex in a series of short sequences where selected guanine bases have been substituted with inosine (I). Time-resolved visible and IR studies reveal that, depending on which guanine is replaced, the yield of photo-oxidation can either increase or drastically decrease. It is proposed that these effects are due to favoured binding at inosine-containing sites. Similar behaviour is observed when IC is replaced with AT, indicating that the complex recognises these steps similarly. These experiments reveal how the photodynamics of a bound complex can be sensitive to changes in one nucleobase, and aid identification of the sites in DNA these compounds target.



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a) Portion of crystal structures of  $\Lambda$ -[Ru(TAP)<sub>2</sub>(dppz)]<sup>2+</sup> intercalated at GC and IC steps (b) TRIR spectra of  $\Lambda$ -[Ru(TAP)<sub>2</sub>(dppz)]<sup>2+</sup> bound to G9- and I9-substituted DNA sequences at 1150 ps after excitation (Keane et al., Chem. - Eur. J., 2017, 23, 10344)

## Vibrational sum frequency generation (VSFG) spectroscopy of electrocatalytic mechanisms

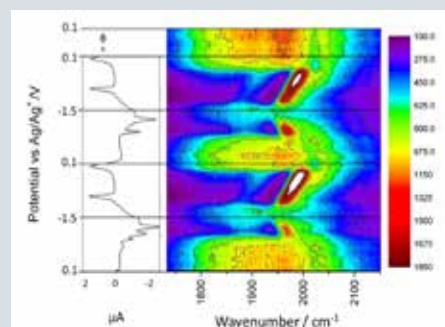
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Here we demonstrate the use of vibrational sum frequency generation (VSFG) spectroscopy to study the mechanisms that occur during electrocatalysis. The 10 kHz broad-band VSFG experiment allows for detection of intermediates present at the surface with only 1 s data averaging. The ability to study short-lived species at electrode surfaces is important as many key intermediates may persist only transiently and be present either at the electrode surface itself or within the electric double layer.

In the study of electrocatalytic H<sub>2</sub> evolution, we are able to identify the formation of a transition metal-hydride complex at the electrode surface even under conditions (low proton concentration) when such behaviour is unexpected. This is significant, as past studies using conventional techniques under

similar conditions have struggled to detect this important intermediate, highlighting the advantage of being able to interrogate the electrode chemistry in situ.



VSFG spectra showing how surface electrochemical events seen by the current-voltage response (left) can be monitored using VSFG spectroscopy (right) where we see new  $\nu(\text{CO})$  bands forming at the potentials of the electrochemical events.

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## Using ANOVA-PCA to facilitate screening of large 2D-IR datasets

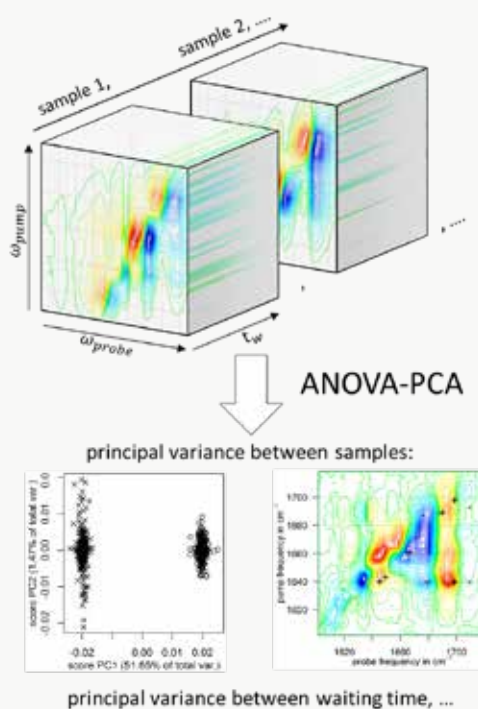
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As a result of recent technical developments at the Central Laser Facility, two-dimensional infrared (2D-IR) spectroscopy has the potential to become a fast analysis tool for studying the molecular dynamics and interactions of biological molecules. Spectral acquisition times are now almost on a par with conventional infrared absorption spectroscopy measurements and so pave the way for larger 2D-IR studies across a broader range of analytes and samples. To address the ever-increasing size and complexity of the resulting 2D-IR datasets, we illustrate an approach to data handling using ANOVA-PCA, a combination of analysis of variance with principal component analysis. This method has been applied in a proof-of-concept 2D-IR screening study investigating the binding of small molecules to 12 different DNA sequences (Anal. Chem 2018, 90 2732–2740). The present report aims to generalise this approach to any 2D-IR dataset.

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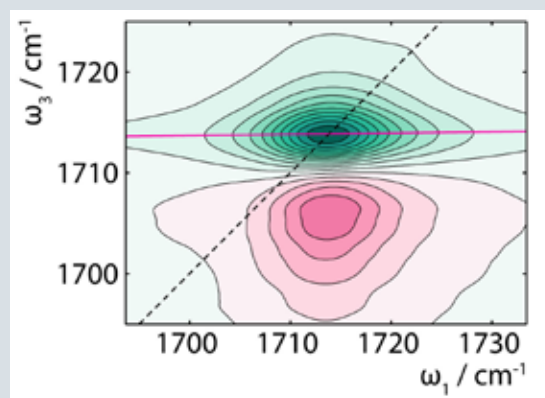


## Investigating electron-phonon coupling and re-orientation effects in hybrid lead-halide perovskites

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Organic cation rotation in hybrid organic–inorganic lead halide perovskites has previously been associated with low charge recombination rates and (anti-) ferroelectric domain formation. Two-dimensional infrared spectroscopy (2DIR) was used to directly measure  $470 \pm 50$  fs and  $2.8 \pm 0.5$  ps time constants associated with the reorientation of formamidinium cations ( $\text{FA}^+$ ,  $\text{NH}_2\text{CHNH}_2^+$ ) in formamidinium lead iodide perovskite thin films. Time-resolved infrared measurements revealed a prominent vibrational transient feature arising from a vibrational Stark shift: photogenerated charge carriers increase the internal electric field of perovskite thin films, perturbing the  $\text{FA}^+$  antisymmetric stretching vibrational potential, resulting in an observed  $5 \text{ cm}^{-1}$  shift. Our 2DIR results provide the first direct measurement of  $\text{FA}^+$  rotation inside thin perovskite films, casting significant doubt on the presence of long-lived (anti-) ferroelectric domains, to which the observed low charge recombination rates have been attributed.



Isotropic 2DIR spectrum for the C–N anti-symmetric stretch vibration of the formamidinium cation in lead iodide perovskite films

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## Femtosecond to microsecond observation of photochemical reaction mechanisms

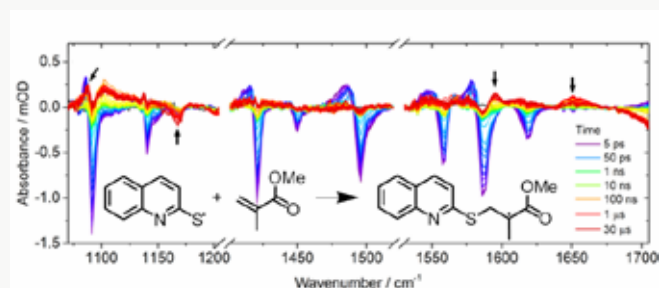
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Transient absorption spectroscopy with the LIFETIME facility allows multiple steps in a sequential reaction mechanism to be observed in a single set of measurements. This capability has been demonstrated for photochemical production of thiyl radicals and their addition to alkenes, a class of reactions increasingly used for click-chemistry in the synthesis of molecules and materials. The same techniques can now be applied to study catalytic cycles initiated by absorption of visible or ultraviolet light.

*Transient infra-red absorption spectra reveal the rates and products of an addition reaction of a thiyl radical to an alkene.*

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## Using surface plasmon resonance excitation to determine real-time distributions of gold nanoparticles in live cells

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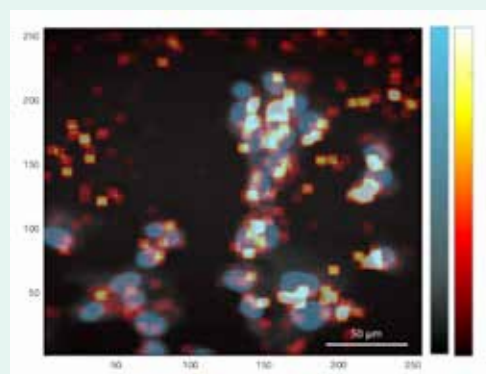
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Heavy atom nanoparticles are increasingly being studied for their potential use in cancer therapy. When localised at a tumour site nanoparticles have been shown to increase the success of traditional radiotherapy due to their dose-enhancing properties. As such, nanoparticles provide a pathway to better patient outcomes using equipment already in place at many medical facilities.

Of all the nanoparticles currently studied, gold nanoparticles, AuNPs, are of specific interest due to their low toxicity and their ability to be functionalised easily

Understanding the physically driven dose enhancement provided by AuNPs is crucial in order to progress toward patient trials. A new method for investigating the uptake dynamics of a nanoparticle in live cell samples in real-time has been demonstrated. Cell membrane association has been shown for multiple formulations of functionalised gold nanoparticle as can be seen above. Additional refinements to this technique allowing imaging to further time points have also been suggested.

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*FLIM and plasmon resonance image of DU145 fixed cell sample 24 hours after treatment with RALA-modified AuNP solution*